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Procedia Engineering 120 (2015) 777 – 780

Procedia Engineering

www.elsevier.com/locate/procedia

EUROSENSORS 2015

Graphene Based Chemiresisitive Vapor Sensors

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Abstract

Graphene based chemiresistive vapour sensors were prepared using interdigital electrodes coated with reduced graphene oxide (rGO). The reduction was performed chemically and thermally. The vapour sensing properties towards toluene, 1-propanol, 2-methyl-5-pentanone or water were investigated after characterisation of the material in dependence of the method of reduction.

Peer-review under responsibility of the organizing committee of EUROSENSORS 2015

Keywords: graphene, chemiresistive sensor, XPS, graphene oxide

1. Introduction

Graphene is a single layer of sp^2 carbon atoms bonded in hexagonal honeycomb crystalline structure. Its extraordinary properties such as large specific surface area and high carrier mobility attract great interest to use graphene as material for ultrasensitive chemical sensors. It is well known, that adsorption of different redox active gas molecules on the graphene surface localize π-electrons and cause a significant increase of layer resistance. [1] Thus it is possible to obtain the changes of layer conductivity among influence of gases. However, sensors for the detection of non-reactive organic volatile compounds have not been studied extensively.

In this work a sensitive layer by reducing graphene oxide through chemical, namely via reaction with ascorbic acid [2] (AA) and physical ways i.e. thermal treatment at temperatures until 1100°C in UHV or Ar/H2 atmosphere was produced. [3] Layers were deposited onto SiO_2 substrates via spin coating or drop coating for further

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Peer-review under responsibility of the organizing committee of EUROSENSORS 2015
doi:10.1016/j.proeng.2015.08.819

investigations (Figure 1). To control the layers thickness, the volume and/or concentration of the graphene based solutions were varied.

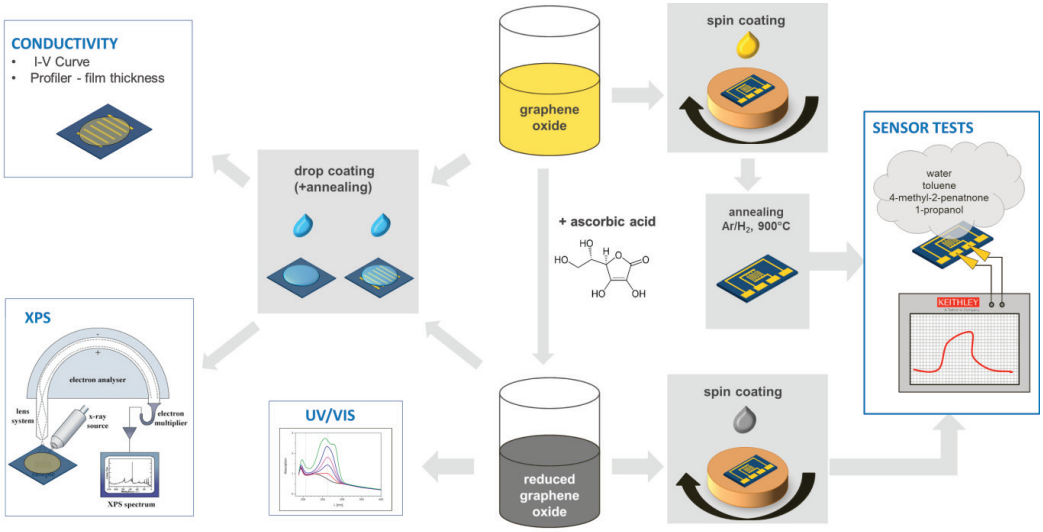

Figure.1: The ways from pristine GO solution to rGO based chemiresistors including characterisation methods.

2. Materials & Methods

As starting material a commercially available aqueous solution, containing 4 mg/ml graphene oxide was used. For chemical reduction via AA, the concentration of GO was set at 0.1 mg/ml, after that, the pH value was adjusted between 9 and 10 using a 25% ammonia solution and the mixture was heated up to 75 °C. After achieving the reaction temperature, ascorbic acid was added to solution in following mass proportion: mAA/mGO = 5. Then the reaction was stopped after 30 minutes by cooling down the mixture in an ice bath. To eliminate the rests of ascorbic acid, the rGO solution was filtered through a polyamide membrane with 0.2 µm pore size. Collected rGO flakes were resolved in DI-water through ultrasonication and filtered again. If necessary, washing procedure can be applied for several times. Subsequently, the pH of washed rGO solution was adjusted again between 9 and 10 by adding several micro liters of 25% ammonia. Taking into account the described procedure and storage of the solution at 4°C, the rGO solution is stable without formation of agglomerates and/or precipitation for several weeks.

Oxidized silicon wafers were used as a substrate material for layer deposition. Piranha and SC1 were applied for cleaning procedure. Afterwards the substrates were treated with acetone in ultrasonic bath (15 min), rinsed with DI-water and placed in an ozone chamber for another 15 minutes. As a result the surface became strongly hydrophilic, which facilitates the deposition via spin-coating of equally hydrophilic GO flakes. To obtain chemically reduced graphene oxide as solid thin films on oxidized silicon substrates, drop casting and drying 30 min at 150 °C was used. Thermal reduction was carried out under Ar/H2 (10:1) atmosphere and at a temperature around 900 °C. Processing steps were as follows: the oven was heated up to 900 °C and purged with Ar/H2-mixture, after that the samples containing GO solid films were placed in the heating zone. After 30 minutes the samples were removed and cooled down to room temperature in Ar/H2 atmosphere.

3. Results and Discussion

UV/vis spectroscopy

A quick method to distinguish between GO and rGO in solutions is UV/vis spectroscopy (Fig. 2). The absorption peak of GO shifts after reduction from 230 nm to approximately 260 nm. Reference measurements of ammonia and ascorbic acid in aqueous solutions have shown that the peak of ammonia lays at 196 nm and AA exhibit a strong peak relatively to rGO at 250 nm. Taking in account this fact, it is advisable to apply the washing process at least

twice, to eliminate the rests of AA and avoid the overlapping of absorptions peaks.
The redshift of the absorption peak of GO after reaction with AA is obvious, which suggests the changes in electronic properties towards graphene due to reduction.

XPS measurements

To investigate the reduction degree with respect to the quantitative chemical composition and bonds, X-ray photoelectron spectroscopy was used. Figure 2 illustrates XPS-spectra from C1s scan of pristine GO and rGO after chemical and thermal reduction, respectively.

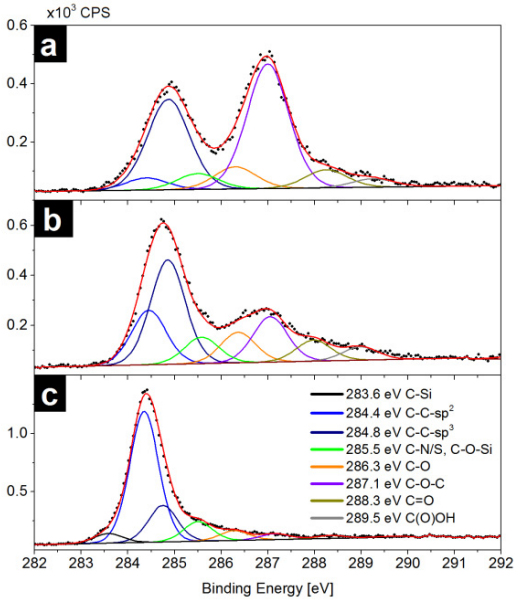

Figure 2: C1s-scans of graphene samples including fits after chemical and thermal reduction

As expected, GO is saturated with oxygen functionalities and almost all of carbon atoms are sp3-hybridized. The majority of functional groups is represented by C-O-C bonds, also known as epoxy groups. Through the reduction the amount of oxygen was decreased and aromatic domains of carbon were recovered, which provides the increase of electrical conductivity and optical absorbance of visible light (color change of GO solution during reduction). It can be observed, that through thermal reduction of GO it is possible to eliminate all other functionalities almost completely. Remaining groups should be located at the edges of graphene oxide, where the binding are more stable. Chemically reduced GO (see Figure 2 b) shows a clear decrease of C-O-C-bonds and an increase of sp^2-hybridized carbon atoms. Based on this fact it can be concluded, that the ascorbic acid opens epoxy groups and eliminates them through a reduction of oxygen. This reaction path is similar to the reduction mechanism of GO with hydrazine. In addition, an increase of C=O and C(O)OH groups relative to pristine GO could be observed in Figure 2b. This indicates the remaining of rests of ascorbic acid.

Chemiresistive Measurements

Using the above mentioned synthesis and characterization methods sensitive layers on interdigitated electrodes were produced. As shown in Fig. 3 they show fast and reversible responses towards various volatile compounds, i.e. toluene, 1-propanol, 4-methyl-2-pentanone or water vapors. The chemically rCO showed higher and more reversible responses than the thermally rGO. This could be due to degradation of the gold electrodes during the temperature treatment by reaction with the substrate in the high temperature fabrication step. However it can be clearly seen that the selectivity of the rGO depends on the degree of reduction. For the chemically rGO, which contains still a higher amount of epoxy groups and is thus more hydrophilic, the strongest responses were observed towards the hydrophilic water. The more hydrophobic thermally rGO showed strongest responses towards 4-methyl-2-pentanone. It is still unclear, why the thermally rGO tends to give chemical responses based on a decrease in the

resistance.

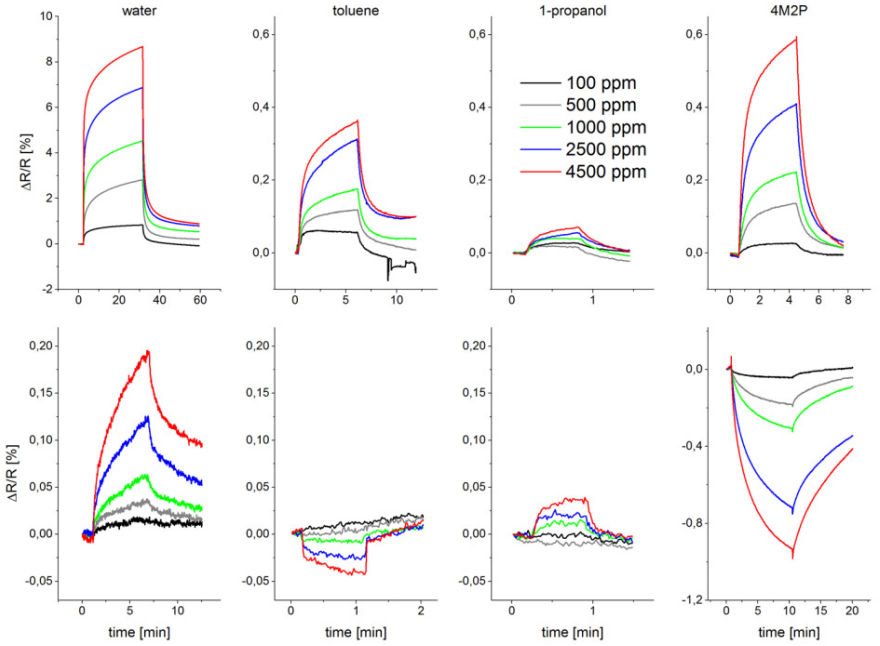

Figure 3: Chemiresistive Sensor responses. Top) chemically rGO. Bottom) thermally rGO

Conclusion

In this study the preparation of sensitive layers based on reduced graphene oxide was shown. We could achieve a deoxygenation of GO by reduction either via a reaction with ascorbic acid, which provides an ecologically friendly and cost efficient process or by thermal treatment. Furthermore, the reduction degree was investigated using XPS and conductivity measurements, which confirmed the restoration of graphene-like properties. We have prepared rGO layers on gold electrodes and shown sensing reaction towards gaseous analytes such as water, toluene, 1-propanol and 4-methyl-2-pentanone. The obtained chemical rGO has established itself as a low noise material with detection limit under 100 ppm for all used analytes.

To gain more insights in the sensing mechanism of rGO towards organic vapors more systematic studies are needed.

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